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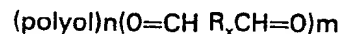
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(54) Method of Producing Difunctional Aldehyde Adducts of Polyol Compounds

(57) The invention concerns the production of resinous adducts by the reaction of difunctional aldehydes, e.g. glyoxal and glutaric dialdehyde, with polyols, e.g. monosaccharides, disaccharides, oligosaccharides and certain polyhydroxyl alcohols in the presence of water. The products are resin-like and, in some instances, have

surfactant properties.

The products have the general formula



where R is a methylene group, x is 0 to 12 and n and m represent variable integers depending on the specific polyol employed.

The products may find uses as molding compounds, bonding agents, crosslinking agents for other polyol compounds and as surfactants.

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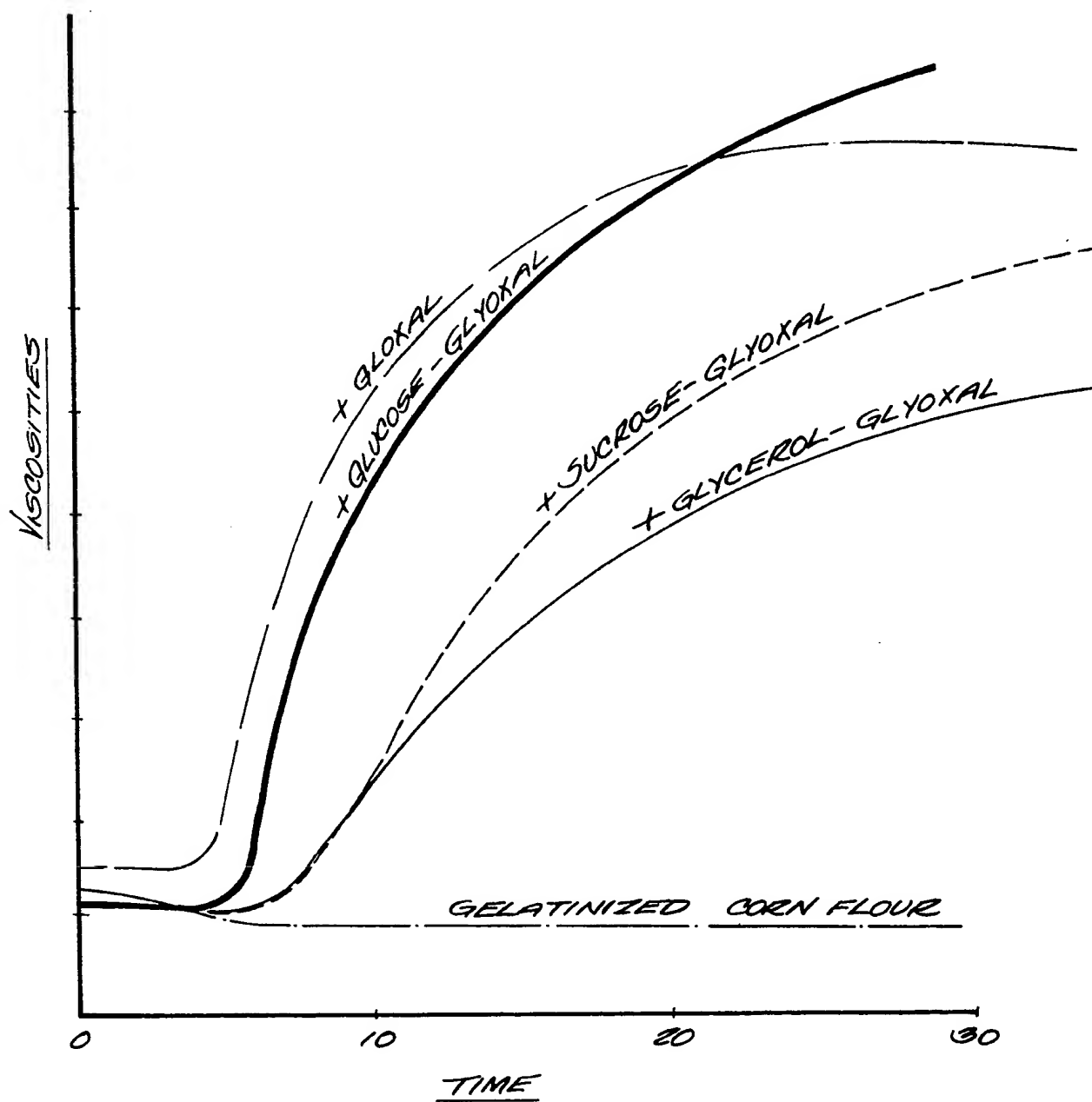
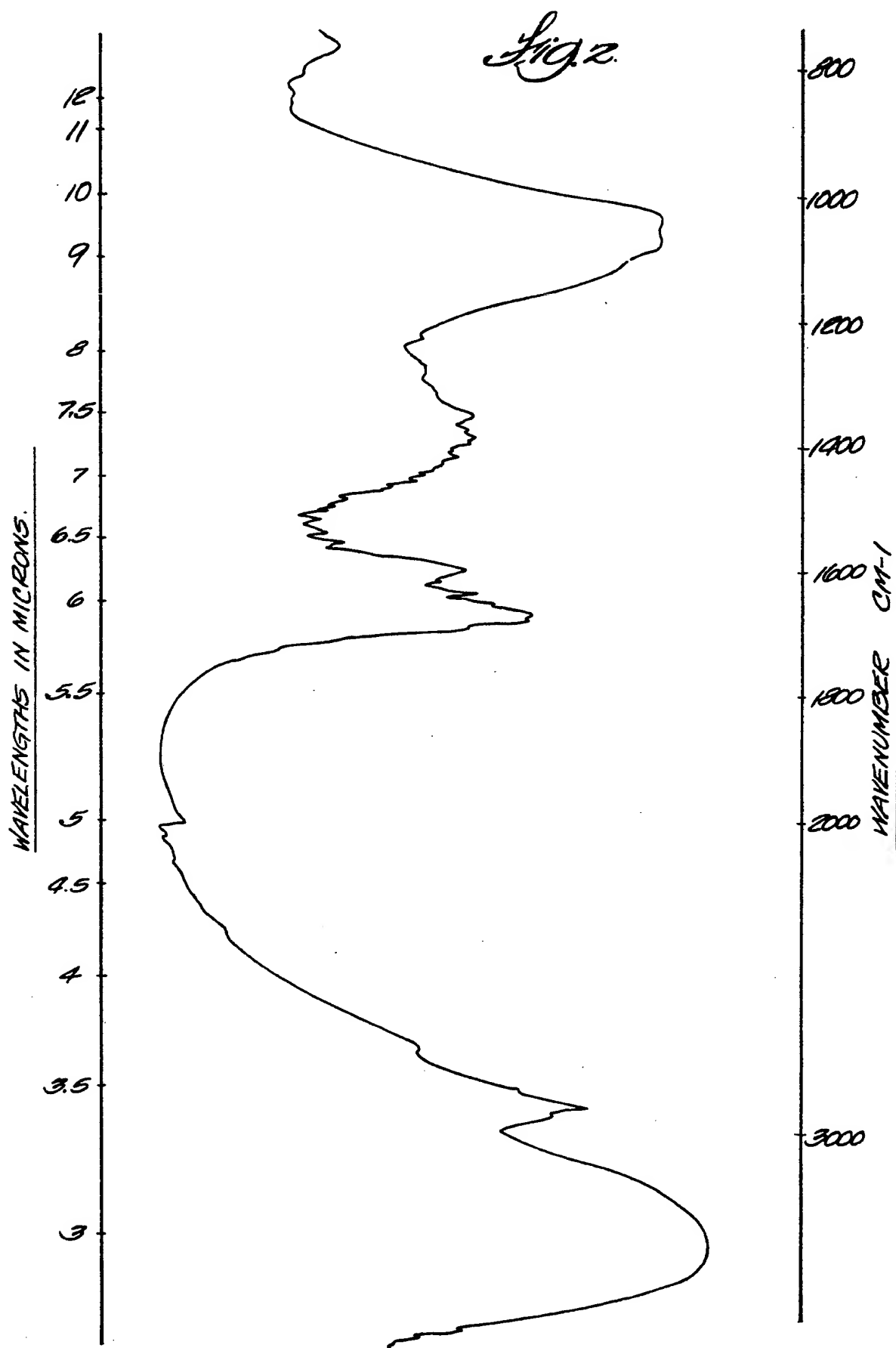


Fig. 1



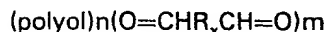
## SPECIFICATION

## Method of Producing Difunctional Aldehyde Adducts of Polyol Compounds

This invention relates to a method of producing difunctional aldehyde adducts of polyol compounds.

5 The crosslinking of polyhydroxyl compounds such as polysaccharides like starches and cereal flours with multifunctional aldehydes is well known in prior art such as U.S. Patent Nos. 2,867,615; 2,999,032 and 3,293,056. U.S. Patent 4,013,629 teaches the use of alkali halides to control the rate of crosslinking between polyols and polyaldehydes in aqueous media. We have now found that the use of the polyoldialdehyde adducts as produced according to the present invention afford an alternate means for control of the polyol crosslinking reaction. U.S. Patent 3,897,503 describes the reaction of 10 alcohols with glyoxal but is directed at the purification of glyoxal rather than the formation of a solid for use as a resin or binder.

15 The present invention relates to the finding that the reaction of difunctional aldehydes such as glyoxal and glutaric dialdehyde on monosaccharides, disaccharides, oligosaccharides and certain polyhydroxyl alcohols, in the presence of water, form molecular compounds having resin-like, and in some instances, surfactant properties. The dialdehyde adducts have the general formula



20 where  $x=0-12$  methylene groups and  $n$  and  $m$  represent variable integers depending on the specific polyol employed. By the process of the present invention, dialdehyde adducts of a number of carbohydrates and polyols are prepared by reacting a monosaccharide, disaccharide or polyhydroxyl alcohol with a dialdehyde in an aqueous solution and then removing the solvent and any excess dialdehyde at or below  $95^\circ\text{C}$  by subatmospheric pressure, heating or desiccation.

25 The products of the present invention have found wide utility as molding compounds, bonding agents, crosslinking agents for other polyol compounds and as surfactants. These products afford a particular advantage over present commercial substances having similar utility in that the saccharide components as used in the present process are derived from renewable resources rather than from petroleum products. In addition, some of these products are biodegradable.

30 In molding compound applications, the solid forms of the polyol-dialdehyde adducts are preferred. These solid forms may be molded as such or may be compounded with fillers, pigments and release agents as is common practice in commercial molding applications. The solid forms or compounded materials may typically be molded under heat and pressure to produce objects of the desired configurations. Generally, molding temperatures of under  $300^\circ\text{F}$  are preferred in order to avoid decomposition of the polyol components. The molding pressures are not critical and may be varied according to the desired density of the final object. In certain cases, the polyol-dialdehyde adducts 35 behave as thermoplastics and thus require mold cooling prior to ejection of the finished part. Several of the products of this invention behave as thermosets and will fully cure to the desired shape so that mold ejection may be accomplished while hot.

40 For bonding applications, the saccharide-dialdehyde adducts may be used in solid, semi-solid or aqueous solution forms. The solid forms may be preferred for blending with particulate materials such as wood flour, wood chips, sand, talc, asbestos and the like whereas the semisolid and aqueous forms are more readily suited to wood flakes, veneers, board laminates and similar applications. Generally, the final bonding process may be accomplished by heating the materials in contact or by heating the materials while under external pressures. The preferred temperatures for effecting the final bond are in the range of  $220$  to  $270^\circ\text{F}$ . In the special case of aqueous forms, bonding may be accomplished at 45 ambient conditions by the evaporation of water.

50 The method of the invention affords a technique for controlling the polyol-glyoxal crosslinking reaction without the use of an alkali halide as disclosed in U.S. patent 4,013,629. Examples of such reaction rate control are illustrated by the viscosity curves as given in Figure 1. This figure compares the rates of viscosity increase when crosslinking a pregelatinized corn flour with aqueous glyoxal versus the same flour with several polyol-glyoxal adducts of the present invention. The curves clearly demonstrate that a saccharide-glyoxal adduct can be selected to give the desired reaction rate for crosslinking polyol materials. This reaction rate control is of great importance when employing polyols with crosslinking agents as thermoset resin systems.

55 A further aspect of the invention is that polyol-glutaric dialdehyde adducts when treated with bases such as ammonium, sodium or potassium hydroxides exhibit marked surfactant properties. These polyol-glutaric dialdehyde products of the present invention may be used as emulsifying agents for incorporating oils into water, air into water or for the removal of dirt from fabrics as typical examples of this discovery.

60 Further objects, advantages and features of the invention will be apparent from the disclosure. Referring to the drawings:—

Figure 1 shows various viscosity-time curves which illustrate reaction-rate control of the polyol-glyoxal crosslinking reaction with various polyols.

Figure 2 is a spectral absorption curve based on analysis of the reaction product of D-Glucose and 40% aqueous glyoxal in accordance with Example 1.

In the preferred preparation of the dialdehyde adducts of the present invention, suitable molar ratios of 1.1 to 1.8 of a polyol such as monosaccharide, disaccharide, oligosaccharide or polyhydroxyl alcohol and dialdehyde are combined with water in a reacting vessel stirred for several hours at ambient conditions, or in some cases, at elevated temperatures. The resulting reaction product may then be subjected to sub-atmospheric pressures in a rotary vacuum or other suitable dryer and the excess water and aldehyde removed under vacuum in the presence of heat until a solid or semisolid residue remains. In some cases oven drying or desiccation of the solid product was substituted for vacuum in order to obtain an anhydrous solid resin. Particularly in adhesive or binder applications, the reaction product may be used in aqueous solution or concentrated to a resin-like syrup mass. When desired, evaporation of the excess dialdehyde and solvent produces, in most cases, a solid glass-like material having little or no offensive odor. Drying temperatures are critical in effecting the degree of post-reaction polymerization. At temperatures higher than 95°C, for greater than 30 minutes, decomposition is encountered.

Representative examples of polyols within the preferred embodiment include:  
straight chain OH compounds having the general formula



in which  $a$  varies from 0 to 10; monosaccharides, disaccharides and higher sugars including polysaccharides, such as amylose, amylopectin and starch; starch containing products, such as cereal flours, derived from cereal grains such as corn, wheat, rice, sorghum, etc.; and related polyhydroxyl compounds such as sorbitol, maltitol, xylitol.

The dialdehyde that is reacted with the appropriate carbohydrate or polyhydroxyl alcohol may be in aqueous form such as 40% aq. glyoxal, or 25% aq. glutaric dialdehyde or may be in a solid form which can be redissolved in water. The comparative amount of dialdehyde combined with a given polyol may vary widely. However, different combining mole ratios may produce final products having different molecular weights and properties. When excess dialdehyde is employed in a given reaction, a maximum quantity of dialdehyde is consumed based upon the available hydroxyl groups and beyond that point the balance of the dialdehyde simply appears as excess free dialdehyde which is then removed during dehydration.

The pH of the reacting solution also has marked effects on the final nature of the product produced. Under highly alkaline conditions, the dialdehydes may undergo self-condensation or Cannizzaro reactions which compete with the desired hemi-acetal and acetal reactions. Thus, neutral or acidic reaction conditions are preferred in order to produce the products of the present invention.

Reaction conditions may vary over a rather broad range of conditions with the carbohydrate or polyhydroxyl alcohol in question. The reaction is frequently carried out satisfactorily under ambient conditions for a time period of 1 to 16 hours. This allows sufficient time for the dialdehyde to crosslink with the carbohydrate or polyol in solution. Reactions in the preferred embodiment of this invention have been successfully carried out at temperatures of 20—104°C.

The following examples demonstrate the preparation and utility of the products of this present invention.

#### Example 1

180.16 g of D-Glucose was combined with 600 ml of 40% aq. glyoxal and 100 ml of water in a reaction vessel. This constituted a 1:5 mole ratio of glucose to glyoxal on a dry basis. The mixture was stirred for 4 hours at 24°C. As the reaction progressed, the reacting solution changed in color from a light yellow to a deep gold. The solution was then reduced in volume by evaporating the excess solvent under sub-atmospheric conditions over a water bath at 60°C. The resulting semi-solid was then heated in an oven at 90°C for 40 hours to produce a clear, amber, glass-like solid. The product was then ground to a fine powder and analyzed for glyoxal content and free acid.

The percent of glyoxal present in the compound was determined using a modification of a procedure suggested in the Union Carbide Corp. Bulletin F-41455, 3—4 (1966) for the volumetric determination of glyoxal. This procedure is applicable to most liquid or soluble solid products containing free or combined dialdehydes and incorporates an alkalimetric titration. The dialdehyde determination consists of adding 1 g of the sample to be tested to 25 ml of 0.1 N aq. NaOH solution and 75 ml of water. The solution is permitted to react for 60 minutes and is then titrated against 0.5 N  $\text{H}_2\text{SO}_4$  using 0.1% alcoholic bromthymol blue indicator to detect the end point. A measurement of the free acid content of the sample is determined by titrating 1 g of the sample in 100 ml of water against 0.01 N aq. NaOH to the appropriate end point. Using these values and the appropriate value for the blank, the % by weight of the dialdehyde can be determined. Analysis of the solid glyoxal-glucose product indicated that 64.05% of the compound by weight was glyoxal. Therefore, the mole ratio of glucose to glyoxal in the final product was 1:5.5.

A sample of the dried product was subjected to I.R. analysis, and the resulting absorption curve

indicated marked differences in comparison to the spectral absorption bands of either glucose or glyoxal. The resulting spectral absorption curve for this product is shown in Figure 2.

#### Example 2

5 In the same manner as described above, 35 g of maltose was combined with 78.75 ml of 40% aq. glyoxal for a mole ratio of 1:7. The solution was stirred for 60 minutes to produce a milky suspension. This constituted an initial mole ratio of 1 mole of maltose to 7 moles of glyoxal. The solution was placed in an oven at 70°C for 90 hours. The final dried product was a pale yellow, glass-like solid with no odor. The product was ground to a powder, screened and heated for an additional 1 hour at 70°C to remove any additional moisture and analyzed for glyoxal content and free acid by the method outlined in Example 1. Analysis of the glyoxal-maltose product indicated that 50.98% of the compound by weight was glyoxal. The mole ratio of maltose to glyoxal in the final product was 1:6.47. IR analysis indicated marked differences in the spectral absorption bands observed in comparison to glyoxal or maltose. 10

#### Example 3

15 In the same manner as described above, 171 g of sucrose was combined with 340 ml of 40% aq. glyoxal for an initial mole ratio of 1:6. The solution was stirred for 1 hour at ambient conditions, then placed in an oven to dry at 71°C for 78 hours. A white gum-like residue remained. This was placed under vacuum desiccation for 64 hours until a dry, clear, glass-like product with no odor was produced. This product was reduced to a powder and analyzed for glyoxal content and free acid by the method outlined in Example 1. Analysis of the glyoxal-sucrose product indicated that 41.89% of the compound by weight was glyoxal. The mole ratio of sucrose to glyoxal in the final product was 1:4.25. IR analysis indicated marked differences in the spectral absorption bands observed in comparison to glyoxal or sucrose. 20

#### Example 4

25 In the same manner as described above, 171 g of lactose was combined with 396 ml of 40% aq. glyoxal and 100 ml of water for an initial mole ratio of 1:7. The solution was stirred for 1 hour and placed in an oven at 71°C for 72 hours to remove water and excess glyoxal. A thick syrup covered by a solid white crust remained. The syrup was then placed on aluminum foil on a glass plate and dried for an additional 68 hours at 71°C. A solid glass-like white solid was produced. This product was reduced to a powder and analyzed for glyoxal content. Analysis of the glyoxal-lactose product indicated that 47.64% of the compound by weight was glyoxal. The final mole ratio of lactose to glyoxal in the final product was 1:5.4. IR analysis indicated marked differences in the spectral absorption bands observed in comparison to glyoxal or lactose. 30

#### Example 5

35 In the manner described above, 50 g of amylose extracted from potato starch was combined with 100 ml of 40% aq. glyoxal and enough water to make 400 ml of solution for an initial mole ratio of 1:2.9. The solution was stirred for 1 hour producing a uniform suspension. Samples were dried under ambient conditions, vacuum desiccation, and in an oven at 71°C for 24 hours. Solid white chip-like flakes formed upon drying. These flakes were hard and appeared to be insoluble in water and ethanol. The solid product was reduced to a powder and analyzed for glyoxal content. Analysis of the glyoxal-amylose product indicated that 38.12% of the compound by weight was glyoxal. The final mole ratio of amylose to glyoxal was 1:1.72. IR analysis indicated marked differences in the spectral absorption bands observed in comparison to glyoxal or amylose. 40

#### Example 6

45 In the manner described above, 61.58 g of glycerol was combined with 125 ml of 40% aq. glyoxal and 54 ml of water for an initial molar ratio of about 2:3. The solution was stirred for one hour at ambient conditions to form a thick syrup. The reaction mixture was then placed in an oven at 92°C for 18 hours. The material dried to a clear glass-like hygroscopic solid. The solid product was analyzed for glyoxal content. Analysis of the solid product indicated that 23.12% of the final product by weight was glyoxal. The final mole ratio of glycerol to glyoxal was 2:1. IR analysis indicated marked differences in the spectral absorption bands observed in comparison to glyoxal or glycerol. 50

#### Example 7

55 In the manner described above, 9 g of D-Glucose was combined with 95.2 ml of 25% aq. glutaric dialdehyde and 5 ml of water for an initial mole ratio of 1:5. The mixture was stirred for 4 hours at ambient conditions. The material was then placed under vacuum desiccation until dry. After 26 hours under reduced pressure, the product was a clear glass-like solid. The product was analyzed for glutaric dialdehyde by titration. Analysis of the product indicated that 18.48% of the sample by weight was glutaric dialdehyde. The final mole ratio of glucose to glutaric dialdehyde was 1:2.5. 55

#### Example 8

60 In the manner described above, 50 g of maltose monohydrate was dissolved in 400 ml of water in a 1 litre round bottom flask. 40.4 g of 40% aq. glyoxal was added to the solution, and the mixture 60

was refluxed with stirring for 4 hours. The initial mole ratio was 0.139:0.278 or 1:2. After refluxing, the solution was reduced in volume to about 75 ml. 100 ml of ethanol was added, and the mixture stirred for 0.5 hours. After standing overnight, the solution was decanted and extracted with ethanol and stored at 45 and 32°F for a number of days. A gum-like solid was precipitated. The filtrate was subjected to vacuum desiccation until a solid, cream colored residue formed. This was dried over anhydrous calcium chloride. The solid adduct had a melting point of 104—106°C. The adduct was analyzed for glyoxal. Analysis indicated that 5.79% of the sample by weight was glyoxal. The final mole ratio of maltose to glyoxal was 1:0.385. IR analysis indicated marked differences in the spectral absorption bands observed in comparison to glyoxal or maltose.

#### 10 Example 9

90 g of D-Glucose was combined with 200 g of 25% aq. glutaric dialdehyde, 1.0 ml. 12 M hydrochloric acid and 300 ml of water in a reflux vessel. This constituted a 1:1 mole ratio of glucose to glutaric dialdehyde. The mixture was stirred for 2.5 hours at 104°C under reflux conditions. During the reaction, color progressed from a clear, to amber, and finally to a very dark brown solution. The solution was removed from the reaction vessel and reduced in volume by evaporation of the solvent under sub-atmospheric conditions in a rotary dryer at a temperature of 70°C, until a black, sticky solid remained. The drying vessel was then placed in an oven at 100°C until a fluid resin was produced. The vessel was then placed in a freezer for several hours. A black solid glass-like resin was then recovered. Subsequently, a sample of the resin was ground to a fine powder and a 20 g charge of the resin was molded in a hot press at 100 psi, 240°F, for 7 min. and then pressed in a cold press at 1000 psi for 15 min. A uniform hard black disc with well defined edges, glossy surfaces and a density of 1.3 g/cm<sup>3</sup> was recovered.

#### Example 10

The powdered resin formed in Example 9 was combined with wood flour in equal proportions by weight and further compounded to contain 12% lampblack and 12% water. A sample was subjected to 1000 psi pressure for 10 min. at 240°F and then to a cold pressure of 1000 psi for 6 min. The resulting molded disc displayed satisfactory physical properties. From this example it is evident that the reflux reaction of glutaric dialdehyde, glucose and hydrochloric acid produces a polymeric resin having thermoplastic molding properties when used alone, or in combination with suitable fillers and extenders.

#### Example 11

90 g of D-Glucose was combined with 72.25 g of 40% aq. glyoxal, 1 ml of 12 M hydrochloric acid and 434.5 ml of water in a reflux vessel. This constituted a 1:1 mole ratio of glucose to glyoxal. The mixture was refluxed at 104°C for 30 hours. At the end of the reaction, the solution had a light brown color. The solution was then subjected to sub-atmospheric conditions in a rotary dryer at a temperature of 85°C and reduced to a syrup. The syrup was then transferred to a freezer. After two days, a thick, sticky amber resin remained. The resin was then transferred to a vacuum desiccator and stored until dry. After dehydration was complete, the glass-like resin was crushed, screened and redessiccated. 20 g of the powdered resin was molded under the same conditions as Example 9. A uniform brown, translucent, hard, glass-like disk was produced.

#### Example 12

500 g of pregelatinized corn flour was combined with 123 ml of 40% glyoxal in a Hobart blender for 45 minutes. The resulting reaction product was air dried at ambient temperatures overnight and then screened through a 20 mesh screen. The glyoxal percentage present in the sample was determined by titration and was found to be 10.15%.

#### Example 13

10 g of maltose was combined with 40 ml of 25% aq. glutaric dialdehyde to form a uniform solution. Ammonium hydroxide was then added to the solution to adjust the pH to 8.2. Color and temperature changes were evident upon addition of the hydroxide. A heavy cream colored precipitate formed in the solution after addition of the hydroxide. The precipitate was filtered from the solution and collected. It was observed that samples of the filtrate and residue when combined with water displayed marked surfactant properties. The product possessed the ability to emulsify oils into water and possessed remarkable persistent foaming properties regardless of water hardness.

#### Example 14

10 g of D-Glucose was combined with 40 ml of 25% aq. glutaric dialdehyde to form a uniform solution. Ammonium hydroxide was then added to the solution to adjust the pH to 8.5. A finely divided cream colored precipitate formed upon addition of the hydroxide. The precipitate was collected by filtration. Experiments with the product indicated surfactant properties similar to those displayed by the product described in Example 13.

**Example 15**

- 10 g of soluble starch was combined with 40 ml of 25% aq. glutaric dialdehyde to form a thick paste. Ammonium hydroxide was added to the paste to adjust the pH to 7.2. Upon addition of the hydroxide, viscosity and color changes took place. A mass of solid curd-like particles formed upon addition of the hydroxide. This material was then separated by decantation, dried and ground into a powder. Experiments with the product indicated surfactant properties similar to those displayed by the product described in Example 13.

**Example 16**

- To a one litre round bottom flask fitted with a heating mantle, stirrer, reflux condenser and thermometer was added 90.0 g of D-glucose, 72.5 g of aqueous 40% glyoxal, 434.5 g of water and 1.0 ml of concentrated hydrochloric acid. The resulting solution was stirred and heated under reflux for four hours. The solution was concentrated under vacuum to yield a yellow syrup of 1.30 g/ml density and a solids content of about 65%.

**Example 17**

- A two litre resin kettle fitted with a heating mantle, a stirrer, a reflux condenser and a thermometer was charged with 870 g of water, 200 g of an acid modified corn flour, 1.0 g of concentrated hydrochloric acid and 40 g of aqueous 40% glyoxal. The resulting dispersion was heated under reflux with stirring for four hours, the resin kettle was adapted for distillation and 500 g of water was removed. The resin dispersion remaining in the kettle was clarified by centrifugation, and the supernatant was further concentrated under vacuum to a solids content of about 50%.

**Example 18**

- A glue was formulated employing ten parts of the resin from Example 16 mixed with one part of fine wood flour. A second glue mix consisted of ten parts of resin from Example 16 and one part of a gelatinized corn flour. These two glues and a commercial 65% solids urea formaldehyde resin were applied at comparable spread rates to both faces of wood core stocks. The wood core stocks were layed upon wood veneer backs and covered with wood veneer facings in a cross-grained direction. These plywood lay-ups were hot pressed under about 200 psi at 270—280°F for 10 minutes. The finished plywood was subjected to dry shear strength testing with the following results:

	Glue Description	Shear psi	
30	Resin of Example 16+corn flour	131	30
	Resin of Example 16+wood flour	196	
	Commercial urea formaldehyde resin	195	

**Example 19**

- The resin syrup from Example 17 was thoroughly blended with coarse wood chips on a 10% resin solids basis. The resulting wood furnish was molded into particleboard under 1000 psi at 280—290°F with a cure time of 10 minutes. The finished particleboard was tested for density and modulus of rupture. The test results are compared to those of *Commercial Standard CS 23—66, Mat-Formed Particleboard* as published by the U.S. Department of Commerce, National Bureau of Standards for particleboard generally made with urea-formaldehyde resin and intended for interior applications.

	Type	Density lbs/cu.ft.	Modulus of Rupture psi	
40	Resin Example 17	62	2660	40
	CS 236066 Class 1	>50	2400	

**Example 20**

- A 16 g quantity of the resin syrup from Example 16 was mixed with 500 g of sand and 7 g of water in a Hobart apparatus for 4 minutes. For comparison, a formulation according to U.S. Patent 4,013,629 consisting of 500 g of sand, 10 g of an acid modified pregelatinized corn flour, 2 g of aqueous 40% glyoxal, 2 g sodium chloride and 13 g water was mixed as described above. Each batch was used to ram several foundry test cores. The resulting test cores were oven cured at 350°F for 12 minutes. After cooling at room conditions, the cores were tested for tensile strength with the following results:

Resin	Average Tensile psi
Example 16	151
U.S. Patent 4,013,629	158

**Example 21**

- Upon reaction with glyoxal, the viscosity of an aqueous dispersion of a pregelatinized cereal flour is found to increase in direct relationship to the rate and extent of the crosslinking reaction which occurs. A recording Brabender Visco/Amlyo/Graph (C. W. Brabender Instruments, Inc., South



Hackensack, N. J.) was found to be ideally suited for measuring these viscosity increases under controlled conditions. In this example, the relative reactivities of several polyol-glyoxal adducts functioning as glyoxal donors were compared to aqueous glyoxal using a standard pregelatinized corn flour as the acceptor. Fifty parts of pregelatinized corn flour was dispersed in 440 parts of water and treated with equivalent amounts of glyoxal based upon the actual titration analyses of the polyol-glyoxal adduct employed. The reaction rates at 40° were then followed employing the recording Brabender instrument. Typical reaction rate curves are shown in Figure 1. The changes in viscosities between the reaction times of 4 minutes and 20 minutes were used as indicators of relative reaction rates. The following table lists the results of these studies using aqueous 40% glyoxal as the standard for comparison.

	Product	Example No.	Weight g	Viscosity Change Brabender Units	Relative Rate	
15	Aq. 40% glyoxal	—	12.8	730	1.00	15
	Glucose-glyoxal	1	9.1	715	0.98	
	Lactose-glyoxal	4	10.0	665	0.91	
	Sucrose-glyoxal	3	10.0	455	0.62	
	Amylose-glyoxal	5	12.3	440	0.60	
20	Maltose-glyoxal	2	10.0	370	0.51	20
	Glycerol-glyoxal	6	12.0	350	0.48	

#### Example 22

Several of the polyol-glyoxal adducts were employed as sources of glyoxal in the preparation of foundry test cores according to the process of U.S. Patent 4,013,629. The mixes consisted of 500 g of sand, 10 g of an acid modified pregelatinized corn flour, 2 g of sodium chloride and 13 g of water. The weights of the polyol-glyoxal adducts were selected to supply amounts of actual glyoxal equivalent to the content of 2 g of aqueous 40% glyoxal. The batches were mixed and the resulting cores were formed and tested as described in Example 20. The results were as follows:

	Product	Example No.	Weight g	Average Tensile psi	
30	Aq. 40% glyoxal		2.0	156	30
	Glucose-glyoxal	1	1.6	192	
	Maltose-glyoxal	2	1.8	192	
	Sucrose-glyoxal	3	2.2	241	

#### Example 23

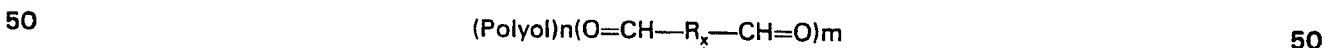
The solid glucose-glyoxal resin from Example 1 was used in the preparation of a white molding power. Forty parts of glucose-glyoxal resin was tumble blended for 90 minutes with 48 parts of alpha cellulose, 10 parts of titanium dioxide and 2 parts of zinc stearate. The resulting white powder was compression molded into discs under 2000 psi at 300°F for 10 minutes. Since the discs were soft and flexible indicating thermoplastic behavior at the end of the 10 minute core, the discs were cold pressed under 600 psi for a further 10 minutes. The finished molded specimens had an average density of 1.55g/cm<sup>3</sup> and an average flexural strength of 4640 psi.

#### Example 24

The corn flour-glyoxal resin, 98 parts, as prepared in Example 12 was blended with 2 parts of calcium stearate as a mold release agent. This blend was compression molded into discs under 1500 psi at 260°F with a cure time of 8 minutes. These discs were hard upon mold ejection indicating the thermosetting character of this resin. The average results for several specimens gave a density of 1.40 g/cm<sup>3</sup> and a flexural strength of 3190 psi.

#### Claims

1. A method of preparing a dialdehyde-polyol adduct having the general formula



where  $x=0-12$  methylene groups and  $n$  and  $m$  represent variable integers depending on the specific polyol employed, comprising the steps of:

(a) combining a polyol in the presence of water with a dialdehyde in a molar ratio of 1:1 to 1:8, respectively;

(b) causing the combination of the polyol and dialdehyde to react for a minimum of one hour at ambient to elevated temperatures;

(c) removing the excess dialdehyde under atmospheric to sub-atmospheric pressures at temperature conditions at 95°C or below.

2. The method of claim 1 wherein the polyol is a saccharide or saccharide containing substance.

3. The method of claim 1 or 2 wherein the dialdehyde is glyoxal.

4. The method of claim 1 or 2 wherein the dialdehyde is glutaric dialdehyde.

5. The method of any one of the preceding claims including a catalytic amount of a mineral acid added to the reaction ingredients. 5

6. The method of claim 2 wherein the polyol is selected from the group consisting of glucose, maltose, lactose, sucrose, glycerol, amylose, and pregelatinized starches and flours.

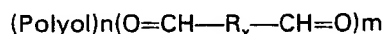
7. The method of claim 4 including the subsequent step of adjusting the pH to above 7.2 by the addition of base.

10. The method of any one of the preceding claims including the subsequent step of subjecting the dried reaction product to temperature and pressure so as to form a molded object. 10

9. The method of claim 1 including the subsequent step of mixing the reaction product of claim 1 with particulate matter selected from the group consisting of cellulosic material, sand and titanium dioxide.

15. The product of claim 9 including the subsequent step of applying heat and pressure so as to form a molded object. 15

11. A method of preparing a dialdehyde-polyol adduct having the general formula



20. where  $x=0, 1, 2$  methylene groups and  $n$  and  $m$  represent variable integers depending on the specific polyol employed; comprising the steps of: 20

(a) combining 40 to 95% by weight polyol in the presence of water with 5 to 60% by weight dialdehyde;

(b) causing the combination of the polyol and dialdehyde to react for a minimum of one hour at ambient to elevated temperatures;

25. (c) removing the excess dialdehyde and water from the reaction to give a solids content of 40 to 70%. 25

12. The method of manufacturing a resin comprising the steps of mixing 40 to 80% polyol with 20 to 60% dialdehyde in an aqueous solution, reacting the components for at least one hour at ambient to elevated temperatures, removing the water from the reaction product, commuting the dried reaction product to a particulate mass and forming the particulate mass into a molded object by the application of heat and pressure. 30

13. A method of manufacturing a molding powder comprising the steps of mixing 40 to 80% polyol with 20 to 60% dialdehyde in an aqueous solution, reacting the components for a minimum of one hour at ambient to elevated temperatures, removing the water from the reaction product, commuting the dried reaction product to a particulate mass, blending 30 to 60% of the particulate mass with 40 to 70% of particulate matter selected from the group consisting of cellulosic material and titanium dioxide and further blending with .01% to 2% of a mold release agent selected from the group consisting of stearic acid and metallic stearic acid salts. 35

14. The method of claim 13 wherein the product of claim 13 is formed into a molded object of the application of heat and pressure. 40

15. A method of making a wood-base fibre or particle panel comprising the steps of mixing 75 to 95% polyol with 5 to 25% glyoxal in an aqueous solution, reacting the components for a minimum of one hour at ambient to elevated temperatures, removing water from the reactants to give a solids content of 40 to 70%, blending 5 to 15% on the solids basis of the product with 75 to 95% wood based material selected from the group consisting of wood chips, wood flour and wood fibre, and forming the blend to a solid object under heat and pressure. 45

16. A method of making a wood adhesive comprising the steps of mixing 75 to 95% polyol with 5 to 25% glyoxal in an aqueous medium, reacting the components at ambient to elevated temperatures for at least one hour, removing water from the reaction to give a solids content of 40 to 70%, blending about ten parts of this concentrated product with about one part of a cellulosic or amylaceous extender. 50

17. An adhesive made in accordance with claim 16.

18. The method of claim 16 including the subsequent step of applying the adhesive of claim 16 to wood and causing the wood to be bonded by the application of heat and pressure. 55

19. A method of manufacturing a foundry core comprising the steps of mixing 75 to 95% polyol with 5 to 25% glyoxal in an aqueous solution, reacting the polyol with the glyoxal at ambient to elevated temperatures for at least one hour, concentrating the reaction product to provide a liquid resin having a solids content of 40 to 70%, mixing the liquid resin with sand, forming the sand mix to the desired shape and causing it to cure to a hardened state. 60

20. A method of manufacturing a foundry core comprising the steps of mixing 40 to 80% polyol with 20 to 60% glyoxal in an aqueous medium, reacting the polyol with the glyoxal for at least one hour at ambient to elevated temperatures, removing the water from the reaction product, commuting the reaction product to a particulate mass, mixing in the ratio of about 1.5 to 2.5 parts of reaction

product with about 500 parts of sand, 10 parts of an acid modified amylaceous material, 2 parts of sodium chloride and 13 parts water, forming this mixture to the desired shape and causing it to cure to a hardened state.

21. A method for controlling the rate of a crosslinking reaction between a polyol and glyoxal comprising the steps of mixing 40 to 80% of a first polyol with 20 to 60% glyoxal in an aqueous medium, causing the first polyol to react with glyoxal at ambient to elevated temperatures for at least one hour, removing the water from the reaction product, commutating the product to a particulate mass, mixing this first polyol-glyoxal adduct with a second polyol and causing the second polyol to become crosslinked at a rate determined by selection of the first polyol. 5
22. A method of manufacturing a surfactant comprising the steps of mixing about 50% of a polyol with about 50% of glutaric dialdehyde in an aqueous medium, precipitating a reaction product by the addition of base to a pH of 7.2 to 8.5, recovering the precipitate from the aqueous medium and drying the recovered precipitate to a solid product having surfactant properties. 10
23. A method of producing difunctional aldehyde adducts of polyol compounds substantially as described herein with reference to the accompanying drawings, and in accordance with any one of Examples 1—24. 15

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